

# Effects of Wet Air and Synthetic Combustion Gas Atmospheres on the Oxidation Behavior of Mo-Si-B Alloys

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## Summary

Continuing our work on understanding the oxidation behavior of multiphase composite alloys based on the Mo-Si-B system, we investigated three alloys in the Mo-Si-B system, designated as A1, A2, and A3. The nominal phase assemblages of these alloys are: A1 = Mo<sub>5</sub>Si<sub>3</sub>B<sub>x</sub> (T1)-MoSi<sub>2</sub>-MoB, A2 = T1-Mo<sub>5</sub>SiB<sub>2</sub> (T2)-Mo<sub>3</sub>Si, and A3 = Mo-T2-Mo<sub>3</sub>Si. Our previous work showed that for exposures to 1100°C, all alloys formed a protective oxide scale in dry air. Exposures to wet air containing about 150 Torr water promoted the formation of a multiphase layer near the scale/alloy interface composed of Mo and MoO<sub>2</sub>. Interrupted mass loss measurements indicated a near zero mass change.

In the present study, isothermal mass measurements were conducted in order to quantitatively determine the oxidation rate constants at 1000°C in both dry and wet air. These measurements are critical for understanding the nature of scale development during the initial exposure, as well as the nature of scale stability during the long-term exposure. Isothermal measurements were also conducted at 1600°C in dry air to make an initial determination of alloy stability with respect to Vision 21 goals. We also conducted alloy oxidation testing in a synthetic oxidizing combustion atmosphere. Alloys were exposed up to 300 hours at 1100°C to a gas mixture having an approximate gas composition of N<sub>2</sub> - 13 CO<sub>2</sub> - 10 H<sub>2</sub>O - 4 O<sub>2</sub>. This gas composition simulates oxidizing flue gas, but does not contain a sulfidizing agent that would also be present in flue gas. The oxidized samples were carefully analyzed by SEM/EDS. This analysis will be discussed to provide an understanding of the role of water vapor and the synthetic combustion atmosphere on the oxidative stability of Mo-Si-B alloys.

## PURPOSE OF THIS PROJECT

The Mo-Si-B system offers a variety of in-situ composite microstructures that possess excellent oxidation resistance, superior creep resistance, and semi-metallic electrical conductivity. Work at Ames has shown that components based on the Mo-Si-B system offer the potential for operating temperatures to at least 1600°C in air. The proposed work concentrates on novel processing and characterization methods to develop alloys for components in heat exchangers and non-load bearing components in gas turbines that can withstand operating temperatures in excess of 1600°C under normal operating conditions for 1000 hours or more.

## DISCUSSION OF CURRENT ACTIVITIES

### ISOTHERMAL OXIDATION IN DRY AND WET AIR

Last year's report discussed the oxidative behavior of Mo-Si-B alloys A1, A2, and A3 in dry and wet air to 1100°C [1]. The alloys were heated in a horizontal tube furnace and interrupted mass measurements were made after specified time intervals for up to 300 hours of exposure in dry and wet air. In the present work, the alloys were prepared into oxidation coupons using the same powder metallurgical technique. Further details of the processing and microstructure of the alloys are omitted and can be obtained from last year's report. In order to quantitatively measure the oxidation rate constants and to assess initial scale formation, oxidation tests were conducted in a vertical tube TGA capable of continuous mass measurements to 1 µg sensitivity. Oxidation coupons were suspended into the furnace retort from a sapphire hangdown wire. Two different vertical tube TGA's were used. The first (dry TGA) is capable of only dry air measurements as the gas flow passes through the balance housing and then over the sample. The advantage of this configuration is that volatile species such as MoO<sub>3</sub> cannot condense onto the hangdown wire and influence the mass measurement. The second (wet TGA) is capable of wet gas measurements and utilizes special glassware that inhibits back diffusion of the wet gas into the balance assembly. The disadvantage of the wet TGA is the possibility for volatile species to condense onto the hangdown wire and to influence the mass measurement. For calculation of rate constants,  $k_p$  denotes a parabolic rate constant, and the units are reported as mg<sup>2</sup>/cm<sup>4</sup>/hr as determined from a plot of mass change versus the square root of time. A linear rate constant is denoted as  $k_l$  and the units are reported as mg/cm<sup>2</sup>/hr. For all isothermal measurements, the reported mass change reflects initial heating from room temperature so that the mass gain and loss of the alloys on initial heating is visible in all plots. The alloys were also tested in a synthetic oxidizing combustion gas (SCG) atmosphere. These tests were conducted using the horizontal tube furnace described in last year's report, with interrupted mass measurements made up to 300 hours of exposure. The SCG atmosphere had an approximate gas composition of N<sub>2</sub> - 13 CO<sub>2</sub> - 10 H<sub>2</sub>O - 4 O<sub>2</sub>. This gas composition simulates oxidizing flue gas, but does not contain a sulfidizing agent that would also be present in flue gas.

Figures 1 and 2 show the isothermal oxidation of Alloys 1 and 2, respectively, in dry and wet air. For both alloys, the interrupted measurement in wet air at 1000°C is shown for comparison. Both alloys show a transition from a steady state linear mass loss at 1000°C to parabolic mass gain at 1600°C. The similarity of the rate constants in dry air between both alloys suggests that at each temperature, the oxidation kinetics for both alloys may be controlled by similar mechanisms. The mass loss at 1000°C likely reflects the slow consumption of Mo from the alloy by evaporation of MoO<sub>3</sub> since boron volatility

is not expected to be significant at 1000°C. The parabolic mass gain at 1600°C reflects the diffusion-controlled transport of oxygen through the glassy scale. The extent of initial mass loss for each alloy is also similar between the continuous and interrupted measurements, and the magnitude of the initial loss increases from Alloy 1 to Alloy 2 with the overall Mo-content of the alloy. A difference is seen between the two alloys for isothermal oxidation in wet air at 1000°C, and this suggests a difference in mechanism between the two alloys. Alloy 1 shows a continued mass loss as seen in dry air, again indicating a continuous consumption of Mo from the alloy. Both the isothermal and interrupted measurements for Alloy 2 in wet air show a steady state mass gain. The positive linear rate constant suggests a reaction rate-limiting process such as the supply of oxidant through the interfacial boundary layer. Further work is needed to investigate this apparent change in mechanism between Alloys 1 and 2 in wet air at 1000°C.

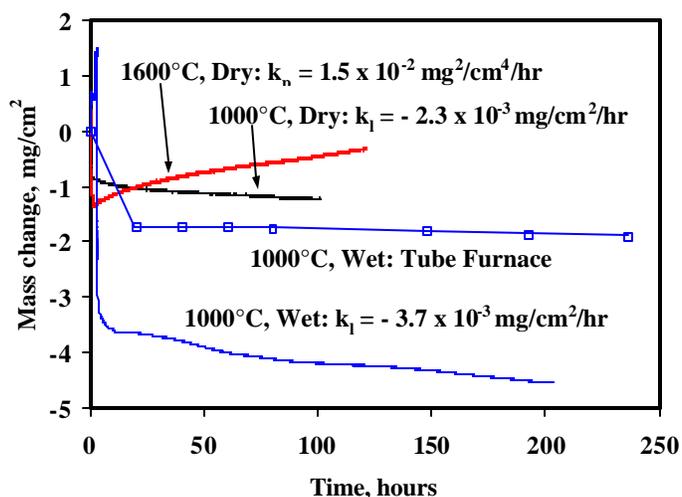


Figure 1: Isothermal oxidation of Alloy 1 in dry air and wet air. Interrupted measurement at 1000°C in wet air is shown for comparison.

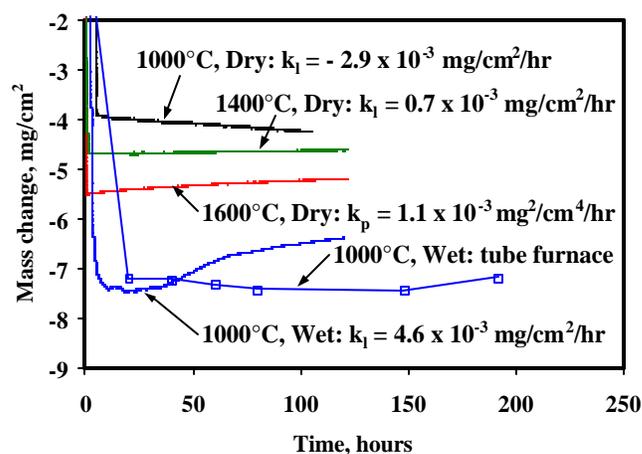


Figure 2: Isothermal oxidation of Alloy 2 in dry air and wet air. Interrupted measurement at 1000°C in wet air is shown for comparison.

Figure 3 shows the isothermal oxidation behavior of Alloy 3 in dry air. The linear rate of mass loss at 1000°C is similar to that measured in Alloys 1 and 2. This may indicate a similarity of mechanism between all three alloys, namely, the reaction rate-limited transport of MoO<sub>3</sub> through the glassy scale. Alloy 3, in contrast to Alloys 1 and 2, continues to lose mass as temperature is increased and never achieves a diffusion-controlled steady state. The rate of mass loss is nearly three orders of magnitude higher at 1600°C compared to 1000°C. Because of the large initial mass loss of at least 40 mg/cm<sup>2</sup> that occurs on initial heating of the unoxidized alloy, MoO<sub>3</sub> condensates on the hangdown wire of the wet TGA and interferes with the measurement of mass. Alloy 3 must first be pre-oxidized in a separate tube furnace to induce the initial volatilization before oxidizing the alloy in the wet TGA. Figure 4 shows that pre-oxidation in dry air for 4 hours promotes formation of a protective scale such that subsequent oxidation in dry air in the wet TGA does not lead to further mass loss. However, pre-oxidation for 4 hours is not adequate to form a sufficiently protective scale for subsequent oxidation in wet air in the wet TGA. The onset temperature for additional mass loss due to MoO<sub>3</sub> volatilization on heating is about

853°C, which is the approximate onset temperature for mass loss on initial heating of the unoxidized material in dry air. Pre-oxidation for 8 hours adequately protects the alloy to prevent additional mass loss on heating in wet air. These observations clearly indicate that initial scale formation on Alloy 3 is heavily influenced by the presence of water vapor. Further work is needed to investigate this effect and to determine if Alloys 1 and 2 show any similar susceptibility.

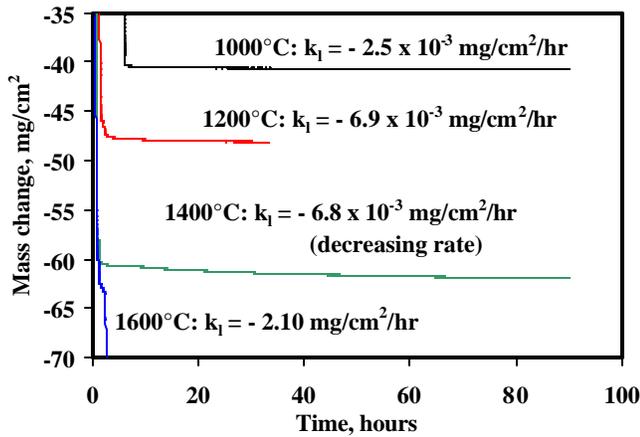


Figure 3: Oxidation of Alloy 3 in dry air. See Fig. 12 for continuation of 1600°C curve. Plot for 1400°C is asymptotic and approximated as linear rate. Data collected from dry TGA that vents MoO<sub>3</sub> away from the hangdown wire.

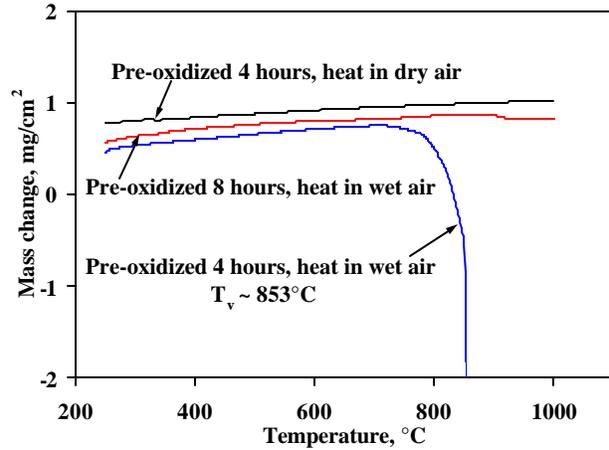


Figure 4: Volatility of MoO<sub>3</sub> during heating of Alloy 3 in wet air depends on the duration of pre-oxidation in dry air. Data from wet TGA that is susceptible to MoO<sub>3</sub> condensation on the hangdown wire.

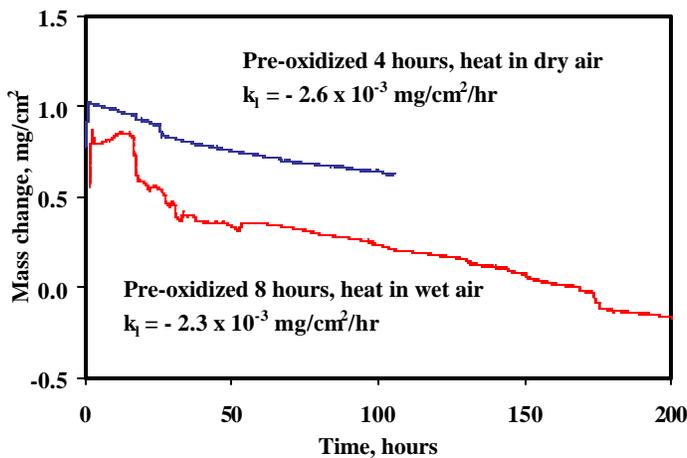


Figure 5: Isothermal oxidation of Alloy 3 in dry air and wet air following pre-oxidation in dry air. These curves are a continuation of two plots shown in Fig. 4.

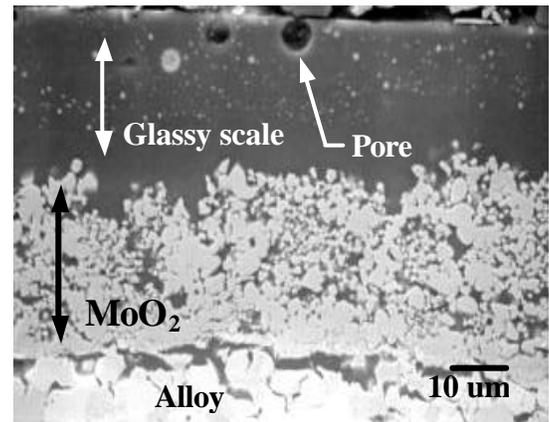


Figure 6: Scale cross-section on Alloy 3 for 8 hrs pre-oxidation in dry air and 200 hrs in wet air. Unoxidized alloy is bright region at bottom, grey region at middle is MoO<sub>2</sub>, and dark region at top is glassy scale.

Figure 5 shows a continuation of two of the curves shown in Figure 4. The rate constant in dry air at 1000°C from Figure 5 is nearly identical to that measured in Figure 3, indicating the repeatability of measurements between the dry and wet TGA. The rate constant in wet air is very similar to that in dry air, again suggesting similarity of the mechanism between dry and wet air at steady state. Figure 6 shows the cross-section of the scale formed on Alloy 3 oxidized in wet air. Although omitted for brevity, the scale cross-section for oxidation in dry air for 200 hours has a very similar appearance. Total scale thickness is 50-60  $\mu\text{m}$ , with nearly equal thicknesses of an outer glassy scale and an interlayer of  $\text{MoO}_x$ . Qualitative EDS precludes the accurate determination of oxygen content as  $x=2$  or  $x=3$ . However, presence of  $\text{MoO}_2$  in the XRD scan from the scale surface is taken as sufficient evidence to identify the interlayer as  $\text{MoO}_2$ . Of interest is the presence of pores containing  $\text{MoO}_x$  within the glassy scale. These are spherical in shape, suggestive of a gaseous species. A wide range of pore sizes can be seen, varying from generally submicron-sized to nearly 10  $\mu\text{m}$ . Figure 6 shows an empty pore that touched the surface, and this observation likely explains the discontinuities in the mass plots of Figure 5. The pores containing  $\text{MoO}_x$  touch the scale/gas interface and are suddenly exposed to air. The ensuing rapid volatilization event leads to a discontinuous decrease in mass. These events are relatively infrequent, based on the fewer number of larger pores. As smaller pores reach the surface in relatively greater numbers than the large pores, they may similarly contribute to the overall steady state mass loss. The existence of filled pores at room temperature suggests the presence of  $\text{MoO}_2$  since the expected volumetric contraction of  $\text{MoO}_3$  on cooling below about 650°C would lead to mostly vacant pores.

Careful examination of the scale cross-sections formed after initial pre-oxidation and after a short subsequent exposure to wet air are shown in Figs. 7 and 8. Figure 7 shows the scale formed on Alloy 3 following pre-oxidation in dry air at 1000°C for 4 hours. A thin section of the unoxidized alloy is visible at the bottom of the micrograph. The scale contains  $\text{MoO}_x$  distributed throughout the external glassy scale. Fig. 8 shows the material from Fig. 7 following a 3 hour exposure to wet air at 1000°C.

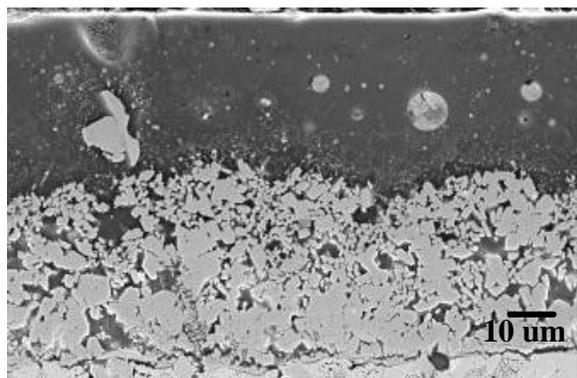


Figure 7: Scale cross-section formed on Alloy 3 after 4 hours pre-oxidation at 1000°C in dry air. Bar = 10  $\mu\text{m}$ .

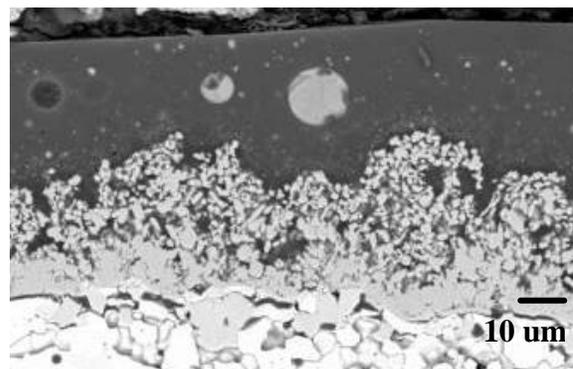


Figure 8: Scale cross-section formed on Alloy 3 after 4 hours pre-oxidation in dry air at 1000°C, followed by exposure to wet air at 1000°C for 3 hours. Bar = 10  $\mu\text{m}$ .

As shown in the TGA plot of Fig. 4, the alloy experienced a significant additional loss of  $\text{MoO}_3$  upon heating, indicating either a short-circuit diffusion path to the underlying alloy and/or the rapid and

extensive movement of trapped  $\text{MoO}_x$  occlusions through the glassy scale on heating. Neither of these possibilities can be discerned from Figure 8, and this indicates that the scale must be examined after a much shorter exposure to wet air following pre-oxidation. Last year's work showed that water vapor contributed to a significant coarsening of the scale, and taken together with the present work, this demonstrates that water vapor promotes the increased transport of oxygen through the scale to promote reaction with the silicide phase components.

There is a possible change in morphology of the  $\text{MoO}_2$  interlayer in Figure 8 where the larger grains following pre-oxidation break up into smaller grains after exposure to water vapor. This may suggest that the top region of  $\text{MoO}_2$  interlayer was converted into  $\text{MoO}_3$  that moved upward through the glassy scale and volatilized from the surface. Careful comparison of Figure 6 to Figures 7 and 8 shows that the morphology and distribution of the  $\text{MoO}_x$  occlusions changes after the extended hold for 200 hours. A band of some 10  $\mu\text{m}$  into the glassy scale nearest the interlayer appears vacant of  $\text{MoO}_x$  occlusions, while at short exposure times in either dry or wet air, the occlusions are distributed throughout the scale. Once the transient mass loss on heating is concluded, the occlusions appear to move slowly through the scale and towards the surface, which leads to both discontinuous and continuous mass losses.

### EXPOSURE TO SYNTHETIC OXIDIZING COMBUSTION GAS

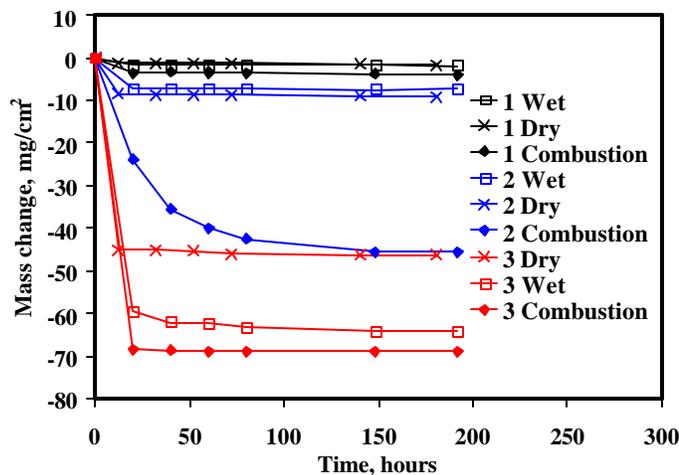


Figure 9: Oxidation of Alloys 1, 2, and 3 in dry air, wet air, and SCG at 1000°C.

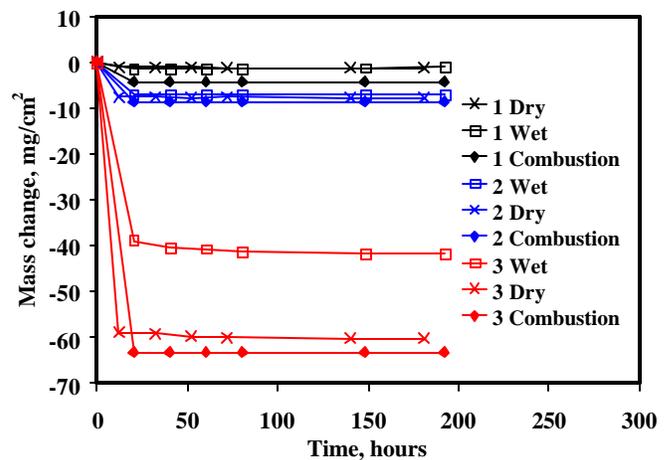


Figure 10: Oxidation of Alloys 1, 2, and 3 in dry air, wet air, and SCG at 1100°C.

As an initial assessment of alloy behavior in a fossil fuel combustion environment, the alloys were also tested in SCG at 1000° and 1100°C, and these results are shown in Figures 9 and 10, respectively. For comparability these plots also show the behavior of the alloys in dry and wet air, as reported last year. While these interrupted measurements cannot accurately assess oxidation rates, they clearly show that Alloy 1 resists the effects of SCG up to at least 1100°C with little difference in comparison to wet and dry air. This is also seen in the scale cross-sections of Alloy 1 in Figs. 11a and 11d. A relatively thin and continuous external glassy scale forms with minimal interlayer. From Figure 10, Alloy 2 appears

resistant to SCG at 1100°C, but the scale cross-section in Figure 11e shows a much more extensive interlayer scale forms underneath a relatively thin external glassy scale. Alloy 2 at 1000°C requires nearly 200 hours to obtain a steady state mass change, and this is reflected in the much different scale morphology seen in Fig. 11b. A thick external glassy layer of 60-70 μm forms with a significant amount of MoO<sub>x</sub> occlusions distributed throughout the layer. The initial mass loss for Alloy 3 appears largest for SCG at both temperatures, although the alloy still achieves a steady state mass change after the initial 20 hour exposure. The scale morphology shown in Figs. 11c and 11f are similar with a thick outer glassy layer containing a high distribution of MoO<sub>x</sub> occlusions. However, the scale at 1000°C is about twice the thickness of that formed at 1100°C. This is similar to the observation in Alloy 2 where the lower temperature exposure nearly doubled the overall scale thickness with a thicker interlayer at 1100°C. Both Alloys 2 and 3 rely upon the T2 phase component to form the protective glassy scale. In contrast, Alloy 1 relies upon the T1 phase component, and its resistance to SCG suggests that the higher boron content of the T2 phase may be more problematic for resistance to SCG and wet air exposures.

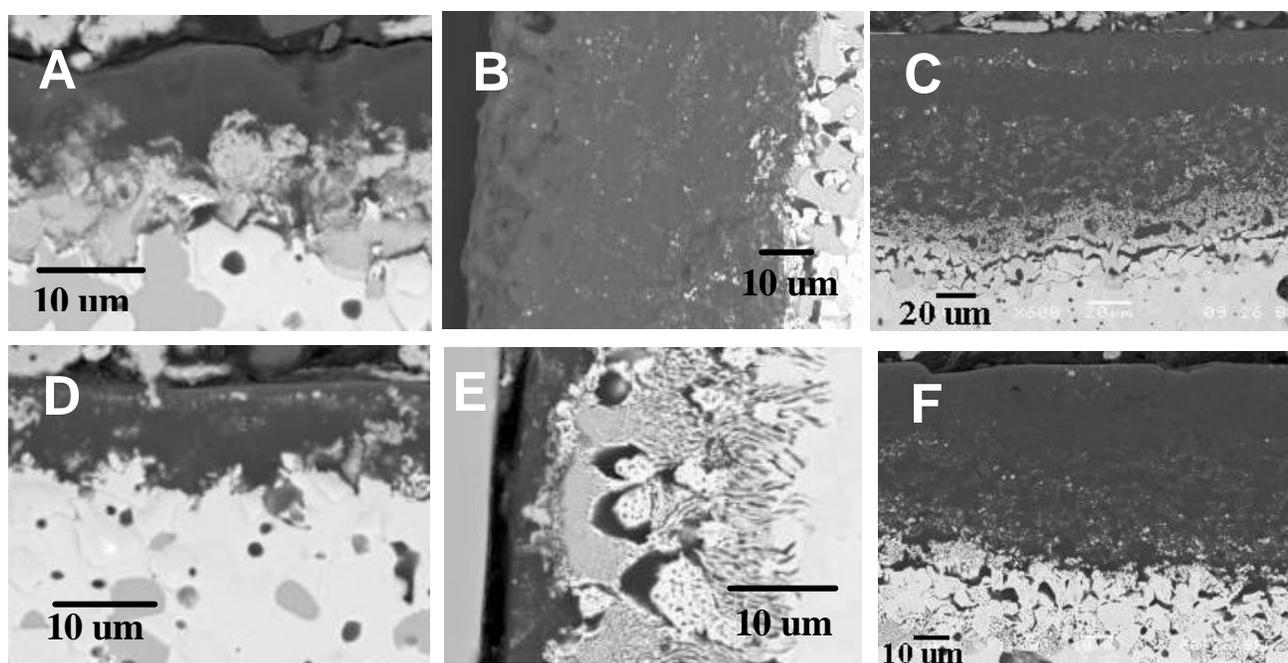


Figure 11: Cross-section of scale formed on alloys following exposure to combustion atmosphere for up to 300 hours. (A) Alloy 1 at 1000°C, (B) Alloy 2 at 1000°C, (C) Alloy 3 at 1000°C, (D) Alloy 1 at 1100°C, (E) Alloy 2 at 1100°C, and (F) Alloy 3 at 1100°C. For Alloys 1 and 3, unoxidized alloy is bright phase along bottom and glassy scale is dark grey phase at the top. For Alloy 2, unoxidized alloy is bright phase at right and glassy scale is dark grey phase at middle-left.

## VISION 21 GOALS

The capacity of Alloy 1 to meet the Vision 21 goals of operation to 1600°C are demonstrated in Figure 12. Both Alloys 1 and 2, which are based on the T1-phase, show excellent resistance to oxidation in dry

air with parabolic rate constants comparable to  $\text{MoSi}_2$  at  $1600^\circ\text{C}$ . Alloy 3 contains a high Mo-content with about 40 vol% bcc-Mo phase. It rapidly oxidizes at  $1600^\circ\text{C}$  with a high rate of linear mass loss, presumably due to the rapid consumption of Mo by the transport of  $\text{MoO}_3$  through the glassy scale. These results, combined with the previous observations of Alloy 2 being susceptible to SCG, show that a great deal of work is required in order to better understand and control the oxidation behavior of Alloy 3. Alloy 1 appears the most suitable candidate for exploitation, and so its potential to function as a protective coating for Alloy 3 must be further investigated.

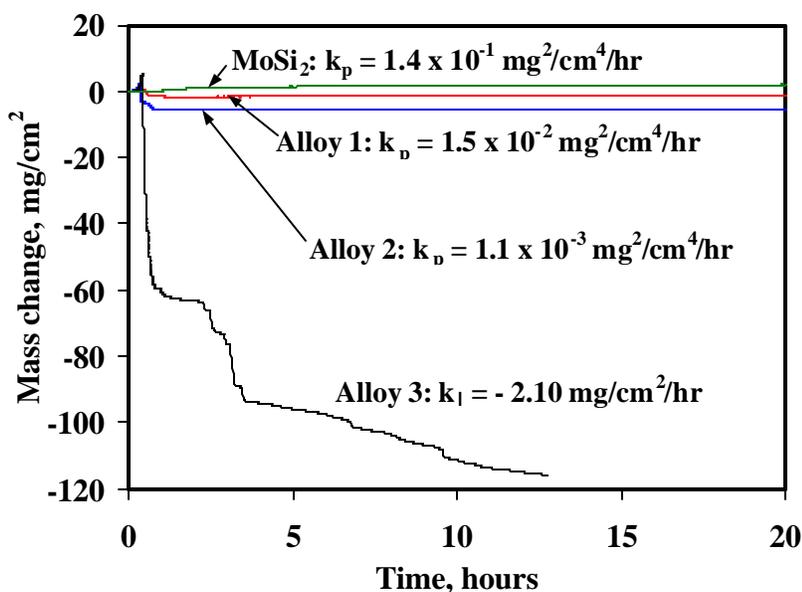


Figure 12: Plot showing mass change for three Mo-Si-B alloys oxidized in dry air at  $1600^\circ\text{C}$ . Also shown for comparison is Kanthal Super® 33  $\text{MoSi}_2$  heating element material.

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1. M.J. Kramer, A.J. Thom, O. Degirmen, V. Behrani, and M. Akinc, "Oxidation Behavior of Mo-Si-B Alloys in Wet Air", Proceeding of the 16<sup>th</sup> Annual Conference on Fossil Energy Materials, Baltimore, MD. Also available from the website link:  
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